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## EXPERIMENTAL STUDIES OF ENERGY STATES ASSOCIATED WITH DISLOCATIONS IN III-V COMPOUNDS

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Résumé - L'analyse des mesures galvanomagnétiques et des spectres d'absorption optique obtenus sur les composés III-V contenant des dislocations montre que les états d'énergie associés aux dislocations dépendent de façon autocohérente de leur taux d'occupation. Dans le cas d'une forte localisation de ces niveaux la position du niveau effectif peut être évaluée dans l'hypothèse du déplacement rigide du niveau neutre, proposé initialement par Read. Dans les autres cas, une description grossière de la position de ces niveaux peut être obtenue en introduisant un paramètre de délocalisation dans le but de diminuer l'amplitude du déplacement rigide de la bande de dislocation.

Abstract - The analysis of transport measurements and optical absorption spectra performed on III-V compounds containing dislocations show that the dislocation energy states self consistently depend on their occupation rate. In the limit of a strong localization of the dislocation energy states, the position of these effective levels can be evaluated by using the hypothesis of the rigid shift of the neutral level as initially proposed by Read. In other cases, a rough description of the effective levels can be obtained by introducing a delocalization parameter in order to reduce the strength of the rigid shift.

I - A SHORT REVIEW

The original idea to associate electron energy states to dislocations in semiconductors came from the experimental pioneer works by Pearson, Read and Morin [1] who established, by means of galvanomagnetic measurements, that dislocations were able to modify as well the free carrier density as their mobility. Analysis of Hall data shew that the occupation statistics of such levels did not possess the same behaviour than impurity levels. Indeed dislocation states are periodically distributed all along the dislocation lines and mix to forme one-dimensionnal energy bands. As a result, trapped carriers can delocalize and transform dislocations into charged wires. Two consequences were expected from the last point : i) trapped carriers interact electrostatically, creating, that way, an extra amount of energy which has to be taken into account for the occupation statistics calculations ; ii) the Coulomb potential of the charged lines was seen, at least for covalent semiconductors to be the main scattering potential for the free carriers.

In very clarifying papers [2,3] Read established, theoretically, the main features for dislocation occupation statistics and its consequences. For a very long period after these papers, any experiment performed on "dislocated" semiconductors was exclusively interpreted in terms of the Read's analysis.

Unfortunately, the screening mechanism of the dislocation potentials initially in-

roduced in the Read's calculation was chosen to be an "extra-ionization" of the impurities located at the vicinity of the dislocation lines. Such a screening mechanism has been recognized, now, not to be the most efficient one. Further modifications were introduced first by Labusch and Schröter [4] who took into account the actual screening mechanism by the free carriers (i.e. the dielectric response of the electron collectivity). A simplest way to evaluate the right screening effects was proposed recently in [5] by direct use of the dielectric function of the material.

Within such theories, Hall effect and conductivity measurements appeared, for a very long time, to be the most powerful tools to detect experimentally energy states associated with dislocations.

Numerous experiments were then performed on covalent semiconductors. First interests for the ionic III-V compounds came later, in the 60's, with the works by Baitinger and Co [6], Willoughby and Co [7,8] on InSb. These first studies were interpreted using Read's model but tried in fact to establish an analogy of the III-V compounds behaviour with covalent semiconductors.

The existence of dislocation "deep" band being well established by such kind of transport measurements, another natural class of experiments to be realized was evidently based on optical properties of materials. Interpreting optical absorption, luminescence or photoconductivity as a result of transitions between all the different states of dislocated materials could, in principle, bring some knowledge on the dislocation state symmetries and therefore would allow a more precise description of the dislocation cores. Such optical investigations were not extensively used for III-V compounds but, when done, brought disappointing results as for instance the absence of luminescence associated with dislocation in Ga As [9] or just poor shifts of the band edges towards lower energies in optical absorption measurements [10][11].

A third class of experiments, based on transient effects at a Schottky barrier was recently introduced in the view to detect dislocation levels and other characteristics, as for instance the free carrier capture cross section. Here again not so many reports of such investigations can be found on III-V compounds. Let us just mention a study [12] on Ga As which, unfortunately tends to conclude to the absence of any deep level associated with dislocations but only to some modification in the strength of different pre-existing DLTS peaks.

So, despite the wide range of experiments which could bring knowledge on dislocation energy states, it is surprising to find out from the literature that, contrarily to covalent semiconductors, not so many simple (or basic) observations are available for III-V compounds (if one excludes the very recent microscopic observations based on the electrical activities of defects such the E.B.I.C. and C.L. methods which are the subjects of other papers at this conference).

Indeed, two main and complexing points distinguish the ionic compounds from the covalent semiconductors, both issuing from the lack on an inversion center.

- a) Symmetry arguments allow one to expect different behaviours for dislocations of equivalent lines but of opposite Burgers vectors. This prevails as well for the plastic properties as for the electronic ones.

The most obvious effect stays evidently in the nature of the atoms at the dislocation cores, which for edge type dislocations are either of A or of B type depending on the Burgers vector sign. Having to distinguish between these two types of dislocations, interest came back for III-V compounds when it was "admitted" [13] (and is still now !) that flexion experiments were capable to introduce selectively each kind of A and B dislocations. This fact was accepted despite the lack of any direct observation of the substructure. Parallely it is still always believed that pure uniaxial compression tests introduce a mixture of any A, B and screw dislocation segments.

Subsequent electrical measurements were then discussed in terms of properties of A or B dislocations [14]. Nonetheless, relatively recent galvanomagnetic measure-

ments [15,16,17] or photoconductivity measurements [18] were interpreted by their authors as showing no electrical activity difference between A or B dislocations (or more exactly between dislocations introduced by opposite flexion experiments).

- b) The other difference with the covalent case, issuing always from the lack of a symmetry center arises from the existence of non vanishing piezoelectric effects. It was shown that (except for screw segments) edge type dislocations must be associated with very strong piezoelectric scattering mechanisms [19,20]. Self consistent calculations of this scattering effect on the free carriers [21] clearly establish that "core" effects (associated with the Coulomb potential of the charged lines) can be neglected when compared to this strain field mechanism.

However, flexion experiments, which are still usually used in the view to introduce A or B dislocations, lead in principle to polygonized substructures which more or less eliminate long range strain fields (depending on the quality of the built-in subgrain boundaries). This fact reacts directly on the efficiency of the piezoelectric scattering and dispersion in conductivity curves does occur.

What, nevertheless, comes out from all these measurements is the fact that transport properties of crystals containing edge type dislocations are coherent with the presence of deep states, the position of their gravity center  $E_0$  (if one, in fact, deals with a multilevel system) can be estimated by representing the dislocation spectrum by only one amphoteric band. This value is seen to stay in the upper part of the energy band gap for InSb [22]. Conductivity and Hall effect are quite well described by piezoelectric scattering mechanisms and occupation statistics calculated with the hypothesis of the rigid shift. Screw dislocations, introduced by standard torsion experiments, are seen to reverse the sign of the free carriers in initially n type InSb [22] ; which indicates the presence of acceptor states very near the top of the valence band. Nonetheless the behaviour of such levels does not seem to follow so well calculations based on the hypothesis of a rigid shift.

Attempts to detect these deep bands associated with edge type dislocations, by optical absorption lead to the following results [10] : measurements never exhibit any deep band but always lead to relatively poor shifts of the band edge towards longer wavelengths. In the case of normally doped samples ( $\sim 10^{14} \text{ cm}^{-3}$ ), the band edge shift increases non linearly with the dislocation density. In the case of more strongly doped crystal ( $10^{16} \text{ cm}^{-3}$ ) this shift becomes rather independent on the dislocation density).

All these observations recalled in this very short review establish quite well that dislocations are probably at the origin of a multi-band system in III-V compounds. But some questions arise naturally from the preceeding description.

- 1) Do the deformation experiments used to introduce dislocation substructures are sufficiently selective to allow one to interpretate the electrical measurements in terms of a difference between A and B dislocation effects ?
- 2) Why do not we observe directly, by optical absorption, the deep levels deduced from transport measurements ? On the contrary, what is the origin of the band edge shift observed even for absorption coefficients as large as about  $100 \text{ cm}^{-1}$  ?
- 3) Do the calculations made for evaluating the occupation statistics fit the observations of any situation as long as one postulates that trapped carriers are strongly localized at the dislocation lines ?

Temptative responses or suggestions to these questions are proposed in the following sections.

## II - AVAILABLE DISLOCATION SUBSTRUCTURES

Direct measurements of the dislocation velocity have established, for a long time, that different A, B or screw dislocation types do not possess the same velocities [23,24]. Such effects of the anisotropic expansion of the dislocation loops could be macroscopically evidenced by means of uniaxial compression tests [25,26] on InSb. Direct observations of the evolution of the dislocation substructure with the deformation, by X Ray Lang topography [27,28,29] establish definitely that, at least for n type undoped InSb ( $n \sim 10^{14} \text{ cm}^{-3}$ ) any compression test was achieved by activation of always the same type of A (or B ?) dislocation half loops, multiplying from surface sources. Difference between the so called "hard" and "soft" cases [29] was seen to arise from the nature and quantity of activated glide systems : in the soft case the expected primary glide system was observed ; in the hard case numerous secondary systems were simultaneously activated.

Differences between the two consequent substructures would correspond : i) to a difference in the dislocation densities, ii) to a higher density of jogs, intersection or reaction in the hard case accompanied probably with a higher concentration of point defects left in the bulk by the dislocation motion.

Quantitative observations of the substructure, by X Ray, show that in the soft case, the screw segments (existing with the two Burgers vector signs) could mutually anneal when the dislocation density increased with the deformation rate and was seen to saturate at a density of about  $10^6 \text{ cm}^{-2}$ . On the other hand edge type segments (because of only one A (or B ?) type) could not anneal since only one sense of the Burgers vector was present. Their density appeared to increase strongly with the deformation rate and was evaluated by T.E.M. observation to reach values as large as  $10^{8-9} \text{ cm}^{-2}$ . This kind of substructure provides a good opportunity to study electrical effects of edge type dislocations of A (or B ?) type.

Macroscopic deformation tests were also performed on Ga As (n type  $10^{15} \text{ cm}^{-3}$ ) in the same way than for InSb. Results [30] show the same macroscopic behaviour of the stress-strain curves with, here also, the occurrence of a hard and a soft case. Although no X Ray topographics could be made (the material being too much absorbing), measurements of the activation parameters indicated the same activation energies for the hard and the soft cases, hint that they result both from the glide of the same A (or B ?) type.

From these observations one emphasizes that this special behaviour is quite general in III-V compounds and that, due to a large difference between the glide activation energie of A and B segments, only one type of these dislocations can be macroscopically introduced in samples by means of deformation tests.

This prevails as well for flexion experiments for which the corresponding "hard" sense of flexion does not correspond to the developement of dislocation of opposite type than the ones corresponding to the "soft" sense of the flexion, but would just correspond to secondary multi-glide systems of the same type than in the soft case.

This very new remark allows one to doubt about any interpretation of the electrical measurements in term of A and B dislocation levels. Let us just remark that our assumption looks to be coherent with the recently observed "identical" electrical activities of dislocations introduced by opposite flexion experiments [16,17,18].

Difference between levels attributed to A and B dislocations [14] may result from differences in the dislocation densities obtained at equivalent deformation (or flexion) rates or to the existence of too numerous unwanted point defects left by the "hard" case deformation mode.

### III - INTERNAL ELECTRIC FIELDS ASSOCIATED WITH DISLOCATIONS

Following the proposal by Read to take into account the electrostatic interaction of the trapped carriers and representing the dislocation by only one amphoteric flat-band, located at  $E_0$  and occupied with a rate  $\xi$  when neutral, it is easy to show that the extra amount of trapped carriers is given by [5] :

$$n_t = 2D \left[ \frac{1}{1 + \exp \frac{E^* - F}{kT}} - \xi \right] \quad (\text{III-1})$$

where  $D$  stands for the density of atomic sites along the dislocation,  $F$  stands for the Fermi level and  $E^*$  is the effective dislocation energy level given by

$$E^* = E_0 + W(n_t) \quad (\text{III-2})$$

$W(n_t)$  represents the derivative versus  $n_t$  of the electrostatic interaction energy of the trapped carriers. This quantity can be evaluated, with a classical electrostatic calculation, when one assumes any carrier strictly localized on (but delocalized along) the dislocation line. The resulting charge line being screened by the free carriers one finds :

$$W(n_t) = \frac{n_t e^2}{2\pi \epsilon_0 \epsilon_L bD} \left\{ \ln \frac{\lambda_G}{b} - \frac{1}{2} \right\} \quad (\text{III-3})$$

where  $\lambda_G$  is the generalized screening wave length and  $b$  the spacing between atomic sites along the dislocation.

Note that formula III-1 with the definition of  $W$  (formula III-3) includes the right feedback effect in  $E^*$  to prevent  $n_t$  from being either too positive (excess of electrons) or too negative (excess of holes). Formula III-1 describes well the amphoteric character of the dislocation "mean" band.

Using (III-1) for interpreting Hall data leads generally to deep values for  $E_0$ . For instance edge type dislocations in InSb are associated with  $E_0$  energy states located in the upper part of the energy band gap. Precise localization of  $E_0$  can not be given since results also depend on the neutral occupation rate  $\xi$  which cannot be made equal to 0.5 as for covalent 60° dislocations.

Absorption measurements on equivalent samples did not detect this deep band but only a shift of the crystal band edge towards lower energies.

Various explanations of such shifts can be found in litterature. In particular in [31], this shift is attributed to the existence of strain fields associated with dislocations, and would increase towards lower energies with increasing dislocation densities. This explanation can be eliminated since, if true, the shift would occur what would be the initial carrier concentration of the investigated samples.

However, experimental results do not show a strong variation of this band edge shift with the dislocation density when the initial carrier concentration reaches

$$10^{16} \text{ cm}^{-3}.$$

Expression III-3 gives, when divided by the electron charge, the amplitude of the built in potentials connected with the dislocation charge at the dislocation core. These potentials extending over a mean length  $\lambda_G$ , which represents the generalized Debye Hückel screening wavelength, correspond to very large internal electric fields. Noticeable Franz-Keldysh effects can be expected from so large fields and would justify the observed shifts of the band edges towards the shortest wavelengths.

However, the self consistent calculation of the  $W$  term [10] shows that when the dislocation density increases,  $W$ , which starts to increase proportionally with the dislocation density, suddenly decreases after a critical value of the dislocation density. This decrease corresponds to the fact that the trapped carriers being more and more dispersed along the dislocation lines interact less and less as soon as the dislocation density becomes sufficiently large. This fact should lead to a decrease of the amplitude of the Franz-Keldysh effect, which fact is not observed experimentally.

Another origin of internal electric fields corresponds to piezoelectric effects. These fields have been calculated to be the most efficient ones for scattering effects and justify, quite well the conductivity measurements in InSb.

Such fields do not decrease in amplitude when the dislocation density increases, contrarily to Coulomb fields associated with the trapped charges. Moreover, the increasing dislocation density, reducing more and more the free carrier density, leads to a decrease of the free carrier screening effects and should correspond to an enhancement of the piezoelectric Franz-Keldysh effects. This corresponds qualitatively to the observation of the band edge shift which looks to increase quicker than the dislocation density.

One therefore suggests that the observed band edge shifts, particularly important in the case of InSb, are actually connected with the existence of internal piezoelectric fields, which are specific to dislocations in III-V (non centro-symmetric) compounds. The non linear increase of these shifts with the dislocation density corresponds to an indirect evidence of the dislocation energy states which reduce, the efficiency of the screening effects, by trapping more and more free carriers when their density increases.

Direct transition from the dislocation levels towards the crystal bands could not be detected by optical measurements. This can be explained by very small values of the optical cross sections associated with each dislocation site. An alternative explanation could be that such transitions would be hidden by the important Franz-Keldysh effects.

Optical absorption measurements in InSb [10] show another indirect evidence of the presence of deep levels associated with dislocations. Intraband absorption, when present in reference samples (case of sufficiently doped crystals) looks to be reduced to values lower than the residual absorption connected with surface effects and is, therefore, no more observed in strongly deformed samples. This can be only understood by a reduction of the free carrier density. At the first order, such a decrease of the intraband absorption has to be proportional to the decrease of the free carrier density. Calculations, based on formula III-1 and 3, of the free carrier density show that the intraband absorption should be always observable even for strongly deformed InSb samples. This suggests that such calculations, made by assuming that the trapped carriers are strongly localized at the dislocation lines, look to under-evaluate the trapped carrier density.

This last remark can also be drawn out from Hall effect measurements performed on InSb containing screw dislocations [22]. Such dislocations are seen to be able to reverse the sign of the Hall effect, establishing, that way, a strong acceptor action of screw dislocation levels. None-the-less, it was not possible to conciliate the behaviour of the conductivity and Hall effect curves with the measured Hall effect inversion temperature, with help of calculations assuming, here again, a strong localization of the trapped carriers at the dislocation lines.

#### IV - DO WE NEED A "DELOCALIZATION PARAMETER" ?

In order to explain the discrepancies between the observed effects and the occupation statistics calculations, let us simply assume that the electrostatic interaction energy leads to a perturbation of the "dislocated" crystal hamiltonian which

can be represented by a self consistent operator  $\hat{W}(n_t)$ .

First order perturbation theory provides the correction in the energy displacement of any crystal state. Representing the dislocation states by the wave function  $\psi_D$ , leads to a modification of the neutral dislocation energy level  $E_0$ , given by :

$$E_D^*(n_t) = E_0 + \int \psi_D^* \hat{W}(n_t) \psi_D d\tau \quad (\text{IV-1})$$

The corrective term represents roughly the mean value of the interaction energy evaluated over the extension domain of the localized states. It is clear that if one considers a strict localization of the carriers at the dislocation line, this corrective term does well correspond to the pure electrostatic energy of a screened charged line (formula III-3). In any other-case, allowing trapped, carriers not to be strictly localized at the dislocation line would give a corrective the formula III-3 and would allow dislocations to be more charged.

In order to evaluate the effect that such a delocalization can have on the occupation statistics, one has [32] evaluated the electrostatic interaction energy by assuming that the trapped carrier density around the dislocation was given by a function of the type :

$$\rho \sim \rho_0 \frac{\exp(-r/r_0)}{r} \quad (\text{IV-2})$$

The parameter  $r_0$  would be characteristic of the delocalization length. Within such an assumption the  $W(n_t)$  term is given by the following formula :

$$\begin{aligned} W(n_t, r_0) = & \frac{n_t^2 e^2}{4\pi \epsilon_0 \epsilon_L D_0} \frac{\xi^4}{(\xi^2 - 1)^2} \left\{ \frac{\xi^2 + 1}{\xi^2 - 1} \text{Log} \left( \frac{1 - e^{-k_G b \xi}}{1 - e^{-k_G b}} \right) \dots \right. \\ & \dots - \frac{1}{2} \frac{k_G b e^{-k_G b}}{1 - e^{-k_G b}} - \frac{1}{2} \frac{k_G b \xi e^{-k_G b \xi}}{1 - e^{-k_G b \xi}} \dots \\ & \left. \dots - \frac{k_G b}{4\xi^3 (\xi^2 - 1)^2} (3\xi^7 - 6\xi^6 - 2\xi^5 + 9\xi^4 - \xi^3 - 4\xi^2 + 1) \right\} \end{aligned} \quad (\text{IV-3})$$

where  $\xi = (k_G r_0)^{-1}$

Applied to the case of InSb shows that, in order to get the right order of magnitude for the intraband absorption decrease, one has to allow trapped carriers to delocalize on about 2 to 3 interatomic spacings.

For screw dislocations delocalization of the order of  $\sim 20$  interatomic spacings are needed to get back a correct simulation of the Hall effect and conductivity curves. The differences in the amplitude of the delocalization between "60°" and screw dislocations are rather coherent with the location of their associated energy states which for the "60°" dislocation look to be rather deep, contrarily to the case of screw for which levels look to stay very near above the valence band getting, that way, a shallow character.



SUMMARY

- 1) Dislocation energy states studies, in ionic semiconductors are noticeably complicated by the existence of different dislocation (A and B) core structures. There is, to our opinion no clear proof which validates the flexion experiments as being able to introduce selectively the wanted A or B dislocations.
- 2) Piezoelectric scattering looks to be the preeminent scattering mechanism. But its efficiency depends on how much the dislocation substructure is polygonized or not. This fact leads to discrepancies in conductivity measurements. Moreover, these fields look to be preeminent ones, as compared with the Coulomb field, to induce the Franz-Keldysh effects observed at the band edge of InSb.
- 3) Occupation statistics calculations show that an eventual delocalization of the trapped carriers around the dislocation line can be considered, specially when dislocation energy states are very near the crystal bands and consequently extend over a large area of the surrounding "perfect" crystal like shallow states.

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